Underground Storage Tank System Field-Based Research Project Report

Submitted to:
California State Water Resources Control Board

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Table of Contents

List of Tables and Figures

Executive Summary

To quantify the probability and environmental significance of releases from petroleum underground storage tank (UST) systems meeting the 1998 upgrade requirements, randomly selected UST systems were tested using a sensitive commercial leak detection method. The test procedure involves the addition of a tracer chemical not normally present in the fuel or the environment surrounding the UST system to the fuel stored in the UST system. After allowing a period of 7-10 days for the tracer to diffuse away from potential leak sources, subsurface vapor samples are collected and analyzed for the presence of the tracer chemical and for petroleum constituents. A total of 182 UST systems were tested in Sacramento County, Yolo County, San Diego County and the city of Temecula.

Releases of tracer chemicals were widespread with detectable levels of tracer being found at one or more sampling probes for 61% of the 182 systems tested while 39% did not release a detectable quantity of tracer. Of the 55 facilities included in the study, 44 (80%) had at least one sample probe with detectable tracer concentrations, while 11 (20%) had no detectable tracer concentration at any probe. All but one of the tracer releases was judged to have been associated with a vapor phase petroleum release. No statistically significant difference in the frequency of these apparent vapor phase releases was observed between double-walled and single-walled UST systems. The one liquid phase release was confirmed to have originated at a joint in single-walled pressurized product piping. The majority of the vapor releases appears to have been associated with upper portions of the tanks at the end of tank nearest the fill riser. The largest tracer releases detected were estimated to have been associated with gasoline releases of 0.4 gallons/day (liquid equivalent), while the vast majority of releases, including the liquid release, are estimated to have been smaller than 0.04 gallons/day. None of the releases observed in the study would likely have been detected by leak detection systems meeting current performance standards of 0.1 gallons/hour (2.4 gallons/day).

The results are a significant improvement over a similar study performed before the implementation of the 1998 upgrade requirements that indicated that 35% of UST systems nationwide exhibited leak rates above 1.2 gallons/day. It should be noted however, that a large but indeterminate fraction of these tank tightness failures were associated with the tank top fittings and would have been detected in this study as vapor releases.

The precise impact of the numerous small releases observed in this study on groundwater quality should be confirmed with more comprehensive hydrogeologic and modeling studies.

Objectives

In response to Senate Bill 989, the California State Water Resources Control Board (SWRCB) initiated a program of field-testing of petroleum underground storage tank (UST) systems. The primary goal of the research program was to "quantify the probability and environmental significance of releases from underground storage tank

systems meeting the 1998 upgrade requirements."[1] In the process of fulfilling this primary objective, the study was also intended to identify the source and causes of releases from UST systems and to document deficiencies in leak detection systems. UST systems meeting the 1998 upgrade requirements can be broadly grouped into three classes. The first group comprises systems with corrosion resistant single-walled tanks and piping. A second group of systems features double-walled tanks and piping. The final group, referred to as hybrid systems, includes a mixture of double and single-walled system components. Because each of these system designs might manifest different probabilities or magnitudes of leakage, an additional goal of the study was to derive independent estimates of leak probability and size for each construction category.

Background

The vast majority of UST systems containing petroleum are used to store motor vehicle fuels and such tanks are therefore the focus of this study. Most facilities have three or four UST systems containing various grades of fuel (e.g., regular, mid-grade and premium unleaded fuels and diesel). A typical UST system includes a fiberglass or cathodically protected steel tank (often 10,000 gallons), a pumping system that conveys the stored product through piping to a dispenser, and additional piping to carry petroleum vapors from the dispensers back to the UST. The purpose of this vapor recovery piping is to minimize the release of petroleum vapor to the atmosphere. Vapor expelled from the UST during product delivery from a tanker truck are captured and returned to the delivery vehicle (Stage I vapor recovery) while vapors that would otherwise be expelled from vehicle tanks that are being fueled at the dispensers are returned to the UST through separate underground piping (Stage II vapor recovery). It is common practice for these vapors to be returned through a single system of recovery lines that interconnect all of the tanks in a common manifold. This allows the vapor space of all the USTs at a facility to function as a single volume. Vent piping may also be interconnected or manifolded in a similar manner allowing all of the tanks to vent through a single pressure/vacuum (PV) relief valve. The UST and its associated product distribution piping is required by installation codes to be emplaced within a clean sand or pea gravel backfill material.

Evidence suggesting that methyl *tert*-butyl ether (MTBE) might be escaping from current generation UST systems provided a major motivation for performing the present work. In a 1999 study conducted by the Santa Clara Valley Water District[2], approximately 50% (13 of 27) of a sample of UST facilities with no known history of MTBE contamination exhibited detectable levels of MTBE in groundwater samples, and approximately 10% (3 of 27) exhibited concentrations of MTBE in groundwater above 25,000 parts per billion (ppb). The 5 highest maximum facility concentrations were 200,000 ppb, 26,000 ppb, 25,000 ppb 6,700 ppb, and 1,700. The higher the concentration the more likely the contamination is due to liquid spills or releases. The remaining facilities with MTBE detections had much lower levels of MTBE, ranging between 0.55 and 800 parts per billion (ppb). These could be from very small liquid spills or releases or from large vapor releases. Interestingly, there was a statistically significant increase in the

[1] California Health and Safety Code Section 25284.1 (a) (1)

[2] Levine Fricke, "Summary Report, Santa Clara Valley Water District Groundwater Vulnerability Pilot Study, Investigation of MTBE Occurrence Associated with Operating UST Systems," Santa Clara, CA, July 22, 1999.

likelihood of detectable levels of MTBE at a facility if the UST system was equipped with an assisted type of stage II vapor recovery system, suggesting that at least some of the releases may have been vapor phase and related to the increased pressures created by assist type systems.

In a follow-up study, 16 of approximately 800 sites known to be contaminated with petroleum products were selected for careful review of the site case histories.[3] The basis for selecting these facilities was the likelihood that new and unreported releases had occurred at the facilities since the facilities had been upgraded in accordance with the 1998 requirements. The site assessment and monitoring data collected at the facilities indicated that a new and unreported release had occurred since the upgrade at 14 of 16 facilities reviewed. A release at the remaining two facilities was considered possible or likely. Confirmatory evidence of any release from any of the UST systems was only available for two of the 16 facilities. One was a reported leak from a primary pipe into a secondary that drained to a containment sump that released the accumulating product for an unknown period. The sump leak detector never alarmed. No leak rate was estimated nor was any effort reported to reconcile the amount of contamination attributed to the new release to the upper limit release rate for the reported mechanism. The other confirmed release in the data set was reportedly a vapor leak. No effort to estimate the magnitude or possible duration of the vapor leak was reported. Confirmation for the release was a report from the facility owner that a vapor leak had been found and repaired. No discussion was provided that attempted to reconcile the maximum possible leak rate with the volume of contamination attributed to the new release.

The finding that detectable quantities of MTBE were present at a significant fraction of UST systems without known histories of contamination suggested that routine release detection methods employed at UST systems were failing to identify releases of potential environmental significance. Such a failure might occur because (1) the release is not "from" the UST system but is a spill at the facility during a delivery, from the dispenser or during a maintenance event while the leak detection is disabled or bypassed, (2) the releases are too small to be detected by conventional leak detection methods, (3) the release occurs from a portion of the system not adequately tested by common leak detection methods (such as vapor phase releases), or (4) problems with the release detection method make it impossible to detect even larger leaks (such as disabled sensors).

Experimental Procedures

Site Selection

Stratified random sampling was performed to obtain a "statistically valid sample."[4] The UST population was stratified both geographically (Northern and Southern California) and by system design (double-walled, single-walled, and hybrid systems). Geographic stratification was intended to adequately represent statewide variation in design and installation practices while minimizing travel time and expenses for the test crews. In this report a UST system is defined as an underground storage tank and its associated product piping. A facility is defined as the property at which a group of

[3] Christine A. Tulloch, "An Evaluation of MTBE Occurrence at Fuel Leak Sites with Operating Gasoline USTs, Santa Clara Valley Water District, Santa Clara, CA, May 2000.
[4] California Health and Safety Code Section 25284.1 (a) (1) (B)

UST systems is located. This report includes results from 23 facilities in Northern California (Sacramento and Yolo Counties) and 32 facilities in Southern California (19 from San Diego County and 13 from the city of Temecula in Riverside County). Testing from a third area, Humboldt and Mendocino Counties is ongoing. The UST system population in California is heavily skewed toward double-walled systems and it was expected that an adequate sample of single-walled and hybrid systems would not be obtained without stratifying by system design.

Databases of registered UST systems were obtained from Sacramento, Yolo, and San Diego Counties by SWRCB staff. The databases were converted into Microsoft Access 2000 format and queries were developed to stratify the records into single-walled, double-walled, and hybrid systems. Single-walled systems were defined as those comprising a single-walled tank and associated underground product distribution piping. Double-walled systems were those that included double-walled tanks and underground product piping. Double-walled systems did not necessarily have complete secondary containment. They typically did not have double-walled vent piping or double-walled vapor recovery piping. Some double-walled systems did not have secondary containment of the fill riser or vapor recovery riser spill buckets. Double-walled systems typically did have under dispenser containment and secondary containment for the submersible turbine pumps. Hybrid systems were defined as any system that did not fit into one of the other two categories. As a consequence, this classification includes systems with single-walled tanks and double-walled piping or double-walled tanks and single-walled piping.

Only systems containing gasoline were included in the random selection pool. However, some systems that contained diesel or other grades of motor vehicle fuel (e.g., high octane racing fuel) were tested because all of the systems (usually three or four) at each facility were tested even though only one of them had been randomly selected. Randomly selected facilities received a letter and a follow-up phone call from SWRCB staff encouraging their voluntary participation in the project. Sites from the city of Temecula were included as part of an ongoing investigation by the Regional Water Quality Control Board. These sites were not randomly selected but, since the contacted group included the entire population of registered facilities in the city, the selections were appropriately representative.

Testing was conducted at all of the selected facilities that signed access agreements and that could be successfully tested. In Sacramento, Yolo and San Diego Counties, 42 (37%) of the 114 facilities that were randomly selected were ultimately tested. In Temecula, the entire UST population was selected and nearly all will ultimately be tested as part of this project (although not all are considered in this report). There were several reasons why not all selected systems were tested in Sacramento, Yolo and San Diego Counties. For 76% of the 72 non-tested systems the owners refused facility access or failed to respond to repeated efforts by SWRCB staff to contact them. In 13% of the cases, non-tested systems were excluded because the facilities had been closed, were currently under construction or were undergoing property transfer. Seven facilities (10%) listed as single-walled in the database were excluded because a review of county files, which are generally more current than the database, indicated they were not single-walled and a sufficient number of double-walled components had already been selected. Finally, one (1%) of the non-tested systems was excluded because floating product was discovered on a very high groundwater table at the beginning of testing. This presented

conditions so markedly different from other sites in the study that the project team chose not to continue the testing.

Of the 182 systems considered in this report, 75% were double-walled, 15% were hybrid and only 10% were single-walled. This uneven distribution occurred despite the stratification by system design. Many of the records in the county databases used to make random selections were outdated or contained incorrect information. A number of the selected single-walled systems had been upgraded to double-walled or had been closed. Both of these effects tended to increase the number of double-walled systems relative to single-walled systems. Inclusion of the Temecula sites further skewed the distribution of sites because there were no single-walled and only 2 hybrid systems among the 43 systems tested.

Field Testing

To satisfy the study objectives it was necessary to investigate the integrity of the selected UST systems. A highly sensitive and reliable investigative approach was needed. It was also desirable to evaluate all of the participating UST systems with a consistent approach so that the results would be comparable. The leak detection method to be used in the field based research program was selected by the principal author (Thomas Young) of the study and SWRCB staff. The selection was based on the experience of the committee, project constraints and third-party certified performance information. Consideration was restricted to portable and broadly applicable testing methods whose performance had been evaluated following US EPA testing protocols[5] and whose evaluation had been reviewed by the National Work Group on Leak Detection Evaluations.[6]

The test methods examined can be divided into those that detect releases based on information collected from inside the UST system (internal methods) and those that detect releases based, at least in part, using information collected from outside the system (external methods). Internal methods can typically only detect releases that are greater than 0.1 gallons per hour during the test. While external methods such as vapor monitoring are capable of greater sensitivity, they are prone to false alarms or significant loss of sensitivity to new releases because of historical releases that have created high background hydrocarbon concentrations near the UST. One approach that avoided these problems and provided the desired level of sensitivity was to use an external method that relies on detection of a non-hydrocarbon tracer chemical added to the fuel in each tank.

Tracer Research Corporation's TracerTight® method was selected for conducting the field tests. This method is the most sensitive one listed by the National Work Group on Leak Detection Evaluations, with a 97% probability of detecting releases greater than 0.005 gallons per hour.[7] Appendix 1 includes a summary of the results of the two

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[5] US Environmental Protection Agency, "Standard Test Procedures for Evaluating Leak Detection Methods" (series of seven documents) EPA/530/UST-90/004, EPA/530/UST-90/005 EPA/530/UST-90/006, EPA/530/UST-90/007, EPA/530/UST-90/008, EPA/530/UST-90/009, EPA/530/UST-90/010, 1990.

[6] http://www.nwglde.org/

[7] Ken Wilcox Associates, "Performance Evaluation of the Tracer Tight Leak Detection System," October 4, 1990. Control Strategies Engineering, "Performance Evaluation of Tracer Tight® as a Complete System Tightness Test," May 1992.

evaluations of the TracerTight® method performed by independent evaluators. Releases smaller than the rate specified in the third party performance evaluations are frequently detectable, but with a lesser degree of reliability. The sensitivity of the tracer method was desirable because it allowed a check on currently used leak detection methods, which are typically required to detect any release greater than 0.2 gallons per hour with a probability of detection of at least 0.95. One of the concerns that motivated the study was that unreported or undetected releases might be responsible for unexplained contamination. Releases below the thresholds of many common release detection methods might be responsible for some of this contamination.

The TracerTight® method of leak detection involves four basic steps. First, subsurface vapor probes are installed around the tanks and piping. Second, a chemical tracer is added to the product stored in the tank, a process known as inoculation. Third, a period of 7-14 days is allowed to permit any tracer chemical released from the system to migrate from the leak source to the sampling probes. Finally, vapor samples are collected from the probe locations and analyzed for the presence of tracer chemicals and total volatile hydrocarbons (TVHC). When multiple UST systems are present at a facility a different tracer chemical is added to each to identify which of the systems was the source of any releases that were discovered. Additional detail about each of the steps in the tracer method follows.

Vapor probes or sampling ports are installed within the tank excavation zone surrounding each tank, along the tank top, and along piping runs (product, vapor recovery and vent lines) to depths typically between 1 and 10 feet. Shallow probes (1-3 feet) are installed near piping runs or along the tops of tanks while the deeper probes (10 feet) are installed between and around tanks within the excavation zone. Sampling probes are spaced no more than 20 feet apart and are constructed of solid PVC piping. For a typical three tank facility, this would result in 8 probes to a depth of 10 feet and 6 probes to a depth of 3 feet within the tank excavation. Probes along the piping runs were placed no more than 20 feet apart. This resulted in 2 to 4 probes along the vent piping trench and several probes along the product piping trenches. Typical probe arrays are shown in the site plans in Appendix 2.

Sampling probes are only open at the end so that when a vapor sample is collected, the sample is known to come from the indicated probe depth. Sampling probes were sealed at the ground surface using a PVC surface completion fitted with a solid removable plug with an o-ring seal. The sampling probe was installed through a hole cored through the concrete. After the sampling probe was placed level with the pavement surface, the core space around the surface completion was filled with a concrete patch to the original thickness of the concrete or asphalt cover.

After sampling probes were installed, the tracer chemical was added to each tank from individual pressurized containers pre-packaged with the amount of tracer needed for the size of the tank. A disposable tube was attached to the tracer container and to the product space within the UST. After the tube was in place, a valve was opened and the tracer was dispensed through the tubing. After any liquid was dispensed and all of the pressure in the container was vented through the tube, the tubing was withdrawn from the tank taking care not to allow the tubing to carry any product from the tank and the container and the connective tubing was carefully placed and sealed within a disposal container. The inoculation procedure was also evaluated during the Control Strategies

Engineering evaluation summarized in Appendix 1. Tracer is added to the product at a level that allows approximately 5 orders of magnitude of dilution in concentration of the tracer from the product liquid or vapor that is released to the lowest detectable levels of the tracer in the test samples.

After the tracer was placed within the tank, a waiting period of 7 to 14 days was allowed for the tracer to escape or be carried out of the UST system with any product release, evaporate from any released product and spread out in all directions into the excavation zone by vapor diffusion. After the 7 to 14 day waiting period, vapor samples were collected from the sampling ports and were subsequently analyzed for the presence of the tracer and total volatile hydrocarbons (TVHC).

Table 1 lists some of the properties of the tracers as compared to the properties of MTBE and benzene. Approximate values are used in the table to protect Tracer Research Corporation's proprietary interest in the identity of the tracers. Note that the tracers are of a similar molecular size and diffusivity, however, the partitioning ratios of the tracers out of gasoline are much higher than for MTBE or benzene. Even though the tracers partition more readily out of gasoline than either MTBE or benzene, the concentration of the tracer in the liquid phase is always greater than the concentration of the tracer in the vapor phase. It is more important to detect small liquid leaks than it is to detect small vapor leaks. However, after being released to the backfill, the tracers are much less water soluble than either MTBE or benzene. Because of this reduced affinity for the water adsorbed to soil particles, the tracers are much more mobile in the soil as a vapor than either MTBE or benzene. The tracers are reliable indicators of whether any product is escaping from the tank, either as a liquid or a vapor.

Table 1. Approximate chemical properties of tracer compounds relative to gasoline

Chemical	Size	Diffusion Rate	Air/ Fuel Partition Coefficient	Air/ water Partition Coefficient
Benzene	1	1	0.0004	0.17
MTBE	1	0.9	0.002	0.011
Tracers	0.6 – 1.1	0.5 -0.7	0.1 – 0.5	10 - 1000

To confirm suspected release sources, in some cases a second tracer test was performed following the detection of a tracer during the initial test. Different tracers were added to each tank during the follow-up testing than were added during the initial test.

Because the method relies on the diffusion of tracer vapors from the release source to one or more sampling locations, an unsaturated, vapor permeable layer between the bottom of the pavement and the top of the water table is required. This was not a

serious factor in this evaluation because all but two facilities were backfilled with pea gravel and only a few of the facilities had water above the bottom of the tanks.

Any release of petroleum below the water table would rise to the surface of the water table, carrying the tracer with it. At the surface of the water table, the tracer has an opportunity to evaporate and spread out as a vapor. While products that are heavier than water and or miscible with water, such as ethylene glycol, would not be guaranteed to rise to the surface of the water, only tanks containing petroleum fuels were included in this study.

Since tanks are not pressurized, tanks that are submerged in water will not release petroleum through the tank wall. The detection of leaks through the wall of a submerged tank relies on the detection of water ingress. Because of the long waiting period associated with this test, and because tank systems are not designed to remove water from the tank bottom, it was easy and convenient to perform a sensitive water ingress test using simple water sensitive paste. This was not a serious factor in this test since only a few facilities in the study included groundwater in the tank excavation above the bottom of the tanks.

Because tracer is added only to the product stored in the tanks and any product released into the backfill from spills or overfills would not contain any of the tracers, the spill buckets around the fill riser and vapor return riser were evaluated in this study using a hydrostatic test. Water was added to the spill bucket and allowed to stand for a few hours. Any change in water level during the stand test was noted as a spill bucket failure. Spill bucket failures were noted in 17.6% of the UST systems tested, but there was no correlation between these failures and either elevated TVHC levels or tracer releases. It appeared likely that the majority of these failures were related to faulty drain valves.

Results

Frequency of Tracer Releases

Releases of tracer chemicals were widespread with detectable levels of tracer being found at one or more sampling probes for 61% of the 182 systems tested while 39% did not release a detectable quantity of tracer (Table 2). The maximum concentration of tracer detected at a facility varied by more than three orders of magnitude from 0.01 to 34.5 micrograms per liter (μg/L). UST systems of different design types exhibited some differences in the percentage that did not release a detectable quantity of tracer, ranging from 33.3% for single-walled systems to 39.4% for double-walled systems. Similar differences were observed in the distribution of the maximum observed tracer concentration for each system type. To determine if the differences between system design types were statistically significant, a nonparametric chi-squared test was used.[8] No statistically significant difference (at the 95% confidence level, $p<0.05$) was observed in the fraction of tracer detections between single-walled, double-walled and hybrid systems. Further, for the systems releasing detectable quantities of a tracer, there was no statistically significant difference ($p<0.05$) in the average maximum tracer concentration between single-walled, double-walled and hybrid systems. A summary of the data from the study is provided in Appendix 3 and site maps of each

[8] Siegel, S. *Nonparametric Statistics for the Behavioral Sciences*. McGraw-Hill: New York, 1956.

facility including probe locations and tracer concentrations above the detectable level are provided in Appendix 2.

Table 2. Summary of maximum tracer concentrations found at UST systems of different design during initial testing

Max. tracer conc., T	Double-walled systems		Hybrid systems		Single-walled systems		All systems	
(μg/L)	Number[a]	Percent[b]	Number	Percent	Number	Percent	Number	Percent
T=ND	54	39.4	10	37.0	6	33.3	70	38.5
ND<T≤0.05	21	15.3	6	22.2	4	22.2	31	17.0
0.05<T≤0.5	27	19.7	3	11.1	6	33.3	36	19.8
0.5<T≤5.0	25	18.2	4	14.8	1	5.6	30	16.5
T>5.0	10	7.3	4	14.8	1	5.6	15	8.2

[a]Number of systems of the specified design and maximum tracer concentration
[b]Percentage of the particular facility type in a particular tracer concentration category

Of the 55 facilities included in the study, 44 (80%) had at least one sample probe with detectable tracer concentrations. The distribution of the detections across facilities provides important information. At 11 facilities (20%) there was no detectable quantity of tracer released from any of the UST systems present. At the other extreme, at 22 facilities (40%) a detectable quantity of a tracer was released from each of the UST systems at the site. These results are significantly different from those that would be expected if the 61% of non-tight systems were randomly distributed among the facilities. In the random distribution case, just two (4.4%) of the facilities would have been expected to have no detectable quantity of tracer released from any system and 11 of the facilities (19.4%) would have been expected to have detectable tracer releases from each of the systems present. This analysis is performed assuming that all sites have the observed average of 3.3 tanks per facility. Facility-wide factors must therefore exist that make it more likely than expected that all of the UST systems at a site are either tight or non-tight. Such factors might include installation problems common to all systems at a facility or commingling of tracer chemicals across systems so that a single release point would result in the release of multiple tracer chemicals. Commingling of tracers can occur when systems are inter-connected by a single manifold, which is the common situation with vapor recovery piping.

Facility-wide correlation in the tracer test results suggests that it may be appropriate to view the data aggregated at the facility level rather than on an individual system basis as in Table 2. Aggregating facilities into the various design categories was straightforward for the 53 facilities where all of the systems were of the same design type (single-walled, double-walled or hybrid). In the remaining two cases, some of the systems were hybrid with the remaining systems being either single-walled (SY14) or double-walled (SD32) so these facilities were classified as hybrid. Table 3 summarizes the results of the facility-level analysis, dividing the results into cases where a tracer release occurred from all of the systems at the facility (F=1), some of the systems (0<F<1), or none of the systems (F=0). Although the results apparently differ between the various types of system construction, notably in the fact that all of the single-walled

facilities had at least one tracer detection, the differences are not statistically significant ($p<0.05$) according to the nonparametric chi-squared test. An alternative way to analyze the same data is to calculate the average fraction of systems with tracer detections at each type of facility. An average of 56% of systems released tracer at hybrid facilities, 60% at double-walled facilities and 77% at single-walled facilities. None of these differences were statistically significant ($p<0.05$) according to a t-test on the means. One reason for the lack of statistical significance in these differences is the small number facilities in the single-walled and hybrid categories.

To summarize the results presented in Tables 2 and 3, there are no statistically significant differences in the probability that a system is not tracer tight among the three most common system designs. This is true whether the results are viewed on an individual system basis as in Table 2 or on a facility basis as in Table 3.

Table 3. Facility-level analysis of test results

Fraction (F) of UST systems at a facility with detectable tracer	Double-walled facilities		Hybrid facilities		Single-walled facilities		All facilities	
	Number[a]	Percent[b]	Number[a]	Percent[b]	Number[a]	Percent[b]	Number[a]	Percent[b]
All detections (F=1)	16	40	4	40	2	40	22	40
Mixed detections (0<F<1)	16	40	3	30	3	60	22	40
No detections (F=0)	8	20	3	30	0	0	11	20

[a]Number of facilities of the specified design and fraction of UST systems with tracer detections
[b]Percent of the particular facility type in a particular detection category

Sources of Tracer Releases

One of the goals of the project was to identify the source of releases from UST systems determined to have all of the system equipment required under the regulations so that future design and installation practice(s) and/or regulations could be modified as necessary. A significant amount of information about the source of a release and the individual system components responsible can be obtained by examining the distribution of tracer concentrations at a facility (Appendix 2), associated TVHC distributions, and the concentration of tracer chemicals in other system components such as sumps and interstitial spaces. Three common scenarios for tracer distributions observed in this study were (1) a smooth decline in tracer concentrations moving outward from a single apparent source typically near the fill riser along the tank top (Facility SD04, Tracer W), (2) a few probes with very low tracer concentrations with all remaining probes having no

detectable concentration of tracer (Facility SY19, Tracer R), and (3) elevated tracer concentrations throughout the excavation zone (Facility SY20, Tracer W).

For nearly all facilities, the majority of tracer detections and the highest tracer concentrations were observed within the tank excavation, with fewer detections and lower concentrations observed in probes located near product piping or vapor return lines. To assess differences in the tracer distribution observed near tanks and piping, the probes at each site were divided into those within and immediately nearest the tank excavation and all others near piping runs. The highest tracer concentration within each of these categories was recorded for each tracer at each facility (Appendix 3). No tracer was detected at 70.3% of the probes near piping compared to 39% for the probes nearest the tanks. Furthermore, the average maximum tracer concentration in probes near piping was 1.13 μg/L compared to 2.26 μg/L for probes nearest tanks. The piping probe with the highest tracer concentration was almost always the one closest to the tank probe with the highest concentration suggesting that even when tracer was detected near piping that the release source was the tank.

The maximum tracer concentration near the piping exceeded the maximum concentration near the tank in just 5 cases. Two of these cases (both at Facility SY14) had tracer concentrations just above the detection limit and very small differences between the piping and tank maximum concentrations (0.014 and 0.012 μg/L) so they are not considered significant. At two other facilities (SD24 and SY38) small releases near the dispenser or from vapor recovery piping provide the most plausible explanation for elevated tracer concentrations. In only one case was there a tracer release that appeared to emanate from the product delivery piping and this source was identified and repaired (See probe 1 result on Tracer A distribution for site SY19, Appendix 2). Very high TVHC levels (>100 mg/L) and moderately high tracer concentrations (0.16 μg/L) were measured in the vapor probe nearest the confirmed release source. The leak was caused by an installation error, the improper cementing of rigid fiberglass piping to an adapter connecting the rigid fiberglass to flexible piping. The leak was at the joint between that adapter and the rigid piping. This was confirmed to be a liquid phase release and was the only liquid phase release identified for either tanks or piping in the study. The frequency of piping (product piping, vent piping or vapor recovery piping) as a source of tracer releases appears to be less than 2% based on these data.

Collectively the results point to vapor containing portions of the UST system, particularly along the tank top, as the source of tracer releases. Three lines of evidence support this finding. First, the highest tracer concentrations were often observed near the fill/vent riser(s) of the tank(s) and in several cases these were the only probes that had detectable tracer concentrations (e.g., Facility SY43, Tracers B and W). Second, no statistically significant ($p<0.05$) distinction in average maximum tracer concentration or release frequency was observed between probes near single and double-walled tanks. Common design elements along the tank top between these two configurations are implicated as potential release sources by this finding. Third, low TVHC concentrations spatially correlated with tracer distributions were observed at many facilities and this is diagnostic of vapor phase releases (see explanation below). Correlated TVHC and tracer distributions were observed for both single and double-walled systems and interstitial tracer concentrations at the double-walled systems were lower than those in the surrounding backfill. Potential sources of vapor only releases from the UST system

include fittings associated with the fill and vapor recovery risers, other tank top fittings such as automatic tank gauging probe and access riser connections, and plumbing associated with vapor recovery systems.

Vapor recovery systems were further implicated as a possible source of subsurface vapor releases by the observation that at some sites where tracer was detected, the individual tracer concentration profiles were spatially correlated, suggesting a common source for the release of tracers originally added to separate UST systems. A distinction can be made between Stage II vapor recovery systems that operate only with pressure supplied by the filling of the automotive fuel tank and offer an unobstructed flow of vapors back to the tank (balanced systems) and those that may involve higher pressures generated by a vapor recovery pump within the system (assist systems). Both types of systems may be subjected to elevated pressures (up to 2.5" H_2O) during a delivery, as a result of vapor growth due to the delivery of product that is warmer than that in the tank, or because of vapor growth required to saturate fresh air drawn into the vapor portion of the system. Assist systems are more likely to lead to pressurization of the UST ullage space for longer periods because of the tendency to return a larger volume of air to the tank than the volume of liquid product withdrawn. This tendency is inherent in the design of many Stage II vapor recovery systems that specify air return to liquid removal ratios (A/L) of between 1 and 1.2.

Information on the vapor recovery systems installed at each of the systems tested in this study was obtained from local Air Quality Management District staff and the results were subdivided into those with balanced and assist systems. Table 4 shows that the two types of vapor recovery systems were nearly equally likely to be associated with a tracer release. However, balanced systems exhibiting a detectable level of tracer showed an average maximum tracer concentration that was lower ($p<0.05$) than that for assist systems.

Table 4. Comparison of test results for balanced and assist Stage II vapor recovery systems during initial facility testing

Vapor Recovery System	Non-detect		Detect		Median detect conc.	Average detect conc.
	Number[a]	Percent[b]	Number	Percent	(μg/L)	(μg/L)
Balance	34	37.4	57	62.6	0.17	1.24
Assist	36	39.6	55	60.4	0.24	3.24

[a]Number of facilities of the specified design and fraction of UST systems with tracer detections
[b]Percent of the particular facility type in a particular detection category

Environmental Significance of Releases

The ultimate environmental significance of releases from UST systems depends on the size of the release (mass rate of product loss from the system), the composition of the product (diesel vs. gasoline, MTBE content), the length of time the release persists, and the travel time required to reach potential receptors. The release status "snapshot" provided in this study does not permit reliable conclusions about release duration, and no

attempt was made to do site characterizations that might answer the question of travel time to receptors. The information collected in the study does, however, permit some conclusions to be drawn about release size and fuel composition. Vapor phase tracer concentrations within the excavation zone provide the most reliable means of estimating the size of the release, but the amount of fuel released with a particular mass of tracer depends on whether the released product was a vapor or a liquid. The tracer chemicals selected and the amount added to the fuel were designed to produce a highly sensitive (<0.005 gallons/hour detectable liquid leak) method of detecting releases. Since the tracers employed are volatile, the concentration in the headspace relative to the fuel concentration is significantly higher than in the liquid phase. Therefore, the method is even more sensitive to vapor phase releases than to liquid releases. It is important to note, however, that despite the high relative tracer concentration in the vapor phase, the majority of the tracer within the UST is always in the liquid phase (except in the extreme of an empty tank).

In all but one case (SY19) tracer detections were judged to have occurred as vapor phase releases. Although this assertion cannot be directly confirmed, it is based on the fact that high tracer concentrations observed at some of the facilities (>5 μg/L) were not accompanied by high TVHC concentrations near the presumed tracer release source and there was no facility-wide correlation between the tracer concentrations and the TVHC concentrations. Higher ratios of hydrocarbon to tracer concentrations are an indicator of a liquid phase release because the ratio of petroleum hydrocarbon mass to tracer mass is much higher in the liquid phase than in the vapor phase because of the volatility of the chemicals used as tracers in this study. Immediately following inoculation and equilibration with the tank headspace, the ratio of TVHC to tracer in the vapor phase above the fuel is in the range of 3 mg/μg while in the liquid phase the ratio is in the range of 700 mg/μg. This ratio can be employed as an approximate indication of whether a tracer release is associated with a vapor or liquid phase petroleum release. Although assignment of releases to vapor or liquid categories is subject to some uncertainty, all releases that were investigated or autopsied during the study confirmed the suspected release mechanism.

To examine the relationship between tracer and TVHC concentrations observed in the field, the TVHC value at the probe exhibiting the maximum tracer concentration was determined for each UST system and the ratio of TVHC to the tracer concentration was plotted as a function of TVHC in Figure 1. Ongoing liquid phase releases are expected to be associated with large ratios of TVHC to tracer concentrations because the mass rate at which TVHC enters the backfill (per unit mass of tracer released) is more than 200 times higher than in the case of a vapor release (upper right quadrant of Figure 1). To a very good approximation all of the tracer released will be found in the vapor phase regardless of whether the release source is liquid or vapor because the tracers are highly volatile, non-sorbing and not subject to biodegradation over relevant time scales. Although the exact values of both TVHC and the TVHC/tracer ratio will depend on a variety of environmental factors, particularly the incidence of past releases (which may elevate TVHC), hydrocarbon biodegradation (which may deplete TVHC), and venting of tracer to the surface or loss to native soil surrounding the excavation zone (which may deplete tracer mass), an ongoing liquid phase release might be expected for sites with TVHC>50mg/l and TVHC/tracer values of >500 mg/μg. Only the release at SY19

(marked in figure 1) meets this criterion in the present study. Similar reasoning has been confirmed by the collective experience of Tracer Research Corporation scientists performing follow-up investigations after the detection of tracer releases at numerous facilities around the world.

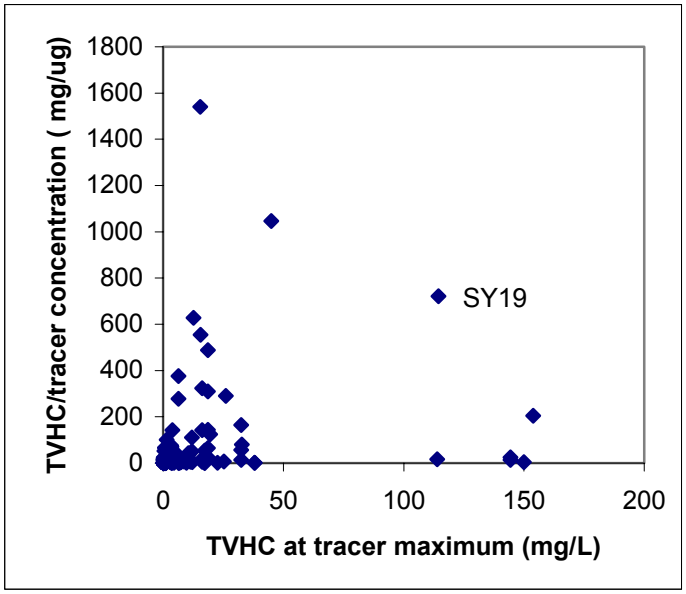

Figure 1. Relationship between the hydrocarbon to tracer ratio and total volatile hydrocarbon concentrations at probes with the highest tracer concentrations

The preceding discussion employs tracer concentrations in calculations without regard to the fact that each of the tanks at a UST facility is inoculated with a different tracer chemical and each of the tracers has somewhat different physical/chemical properties. It is important to check whether any systematic biases can be observed in the results based on the identity of the tracer chemical. The TracerTight® method adjusts for the volatility difference between tracers by adding each tracer to the liquid product at a concentration calculated to produce equivalent initial vapor phase concentrations. To test whether there were any systematic differences in maximum observed concentrations among the four tracer chemicals used in this study, average and median levels of the maximum observed concentration at each site were calculated (Table 5). No statistically significant difference ($p<0.05$) was observed in the detection frequency or the average maximum tracer concentration among any of the four tracer chemicals employed in the study.

Table 5. Comparison of the results obtained using four different tracer chemicals during initial facility testing

Tracer	Non-detect		Detect		Median detect	Average detect
	Number [a]	Percent [b]	Number	Percent	(μg/L)	(μg/L)
A	18	36.0	32	64.0	0.53	1.79
B	14	31.1	31	68.9	0.24	3.55
R	22	48.9	23	51.1	0.35	2.39
W	16	38.1	26	61.9	0.11	1.06

[a]Number of UST systems inoculated with the specified tracer with detect or non-detect results
[b]Percent of UST systems inoculated with the specified tracer with detect or non-detect results

To determine the potential environmental significance of the tracer releases observed in this study, the amounts of gasoline and MTBE that might be released in conjunction with the largest tracer releases were estimated. The calculations involve (1) estimating the total mass of tracer released to the tank excavation zone, (2) estimating the tracer concentration within the tank headspace during the period of the release, and (3) approximating the release duration. These three factors are combined to derive a leak rate estimate according to the following:

$$R_L = \frac{f \cdot C_{TE} \cdot V_E}{C_{TH} \cdot t_L \cdot 1000 \frac{gal\ vapor}{gal\ liquid} \cdot 3.785 \frac{L}{gal}} \quad (1)$$

where R_L = liquid equivalent volumetric leak rate required to produce the observed tracer distribution (gal/hr)
f =fraction of excavation zone containing tracer (dimensionless)
C_{TE} = average concentration of tracer within excavation zone (μg/L)
C_{TH} = initial concentration of tracer within the tank headspace (μg/L)
V_E = total pore volume within the tank excavation zone (L)
t_L = time period over which the observed tracer distribution was generated (hr)

Each term in equation 1 involves approximations but the result should be accurate to within an order of magnitude and are certainly reliable as a lower bound for the amount of product released into the backfill during the test. The fraction of the excavation zone that contains tracer, f, is estimated from the fraction of vapor probes within the tank excavation zone that have detectable tracer concentrations. The average tracer concentration within the excavation, C_{TE}, is a volume-weighted average of the probes with tracer detections within the tank excavation. The concentration of tracer within the tank headspace, C_{TH}, is a calculated value based on the tracer concentration within the fuel at the time of inoculation, an assumed half-full tank and an equilibrium distribution of the tracer between the fuel and the headspace. C_{TH} therefore represents a likely maximum concentration of tracer in the headspace because fuel deliveries subsequent to

inoculation will dilute the tracer concentration in the fuel and in the headspace. The excavation volume, V_E, is calculated assuming a 14' depth and 2' of space between adjacent tanks and between each tank wall and the excavation boundaries. The pea gravel in the excavation zone is assumed to have a porosity of 0.30. The period of a leak is generally assumed to be the time between inoculation and collection of the vapor sample unless the maximum tracer concentration has moved significantly beyond the source zone suggesting that a shorter time period should be applied. The factor of 1000 in the denominator represents an approximate ratio of the gaseous to liquid volume for a particular mass of gasoline. The calculation approach also assumes that tracer does not escape the excavation zone to the atmosphere or to soil beyond the excavation zone.

Equation 1 was applied to estimate leak rates for the sites within Sacramento and Yolo Counties that exhibited the highest tracer concentrations in order to delineate the potential extent of the problem. Estimated liquid equivalent leak rates ranged from 0.0002 to 0.4 gal/day for the 13 facilities with the largest tracer releases. The high end of this range was for site SY08, which showed unusually high tracer concentrations. None of the other facilities in Sacramento and Yolo Counties had estimated leak rates above 0.04 gal/day. All of the remaining facilities in Sacramento and Yolo Counties are likely to have release rates near or below the lowest end of this range. The smallest detectable vapor release rate in the study was in the range of 0.00001 gal/hr of liquid gasoline equivalent. Employing a similar calculation approach, the liquid phase release detected at SY19 exhibited probable upper and lower bounds between 0.004 and 0.1 gal/day. To put these numbers in perspective, the required detection limit for leak detection methods that operate monthly is 0.2 gal/hr or 4.8 gal/day, 50 times higher than the upper limit for the only liquid release found at SY19 and 10 times higher than the estimated equivalent liquid release rate of the vapor release found at SY08. However, a release at the high end of the range of estimated rates observed in this study would result in the discharge of nearly 0.5 lb/day of MTBE into the environment, assuming that the MTBE in fuel behaves as an ideal solution and that the MTBE volume fraction in the fuel is 0.1. Detailed modeling studies are required to determine the potential groundwater impacts of MTBE releases of this magnitude.

It is important to realize that, despite the frequency of releases observed in this study, the environmental problems associated with UST systems are significantly less than they were before the 1998 upgrade requirements became effective. EPA conducted a national survey with a random sample of UST systems using a volumetric tank tightness test method with a detection limit of 0.1 gallons/hour and found that 35% of over 450 tank systems failed the test.[9] Based on the estimates of release magnitude presented above, none of the 182 systems tested would have been expected to fail a similar test.

Retest Results

To further confirm release sources, owner/operators of all facilities at which one or more tracers were detected were given an opportunity for a second tracer test following repair of their systems. Re-tests were completed for 34 UST systems at 13 facilities in Sacramento and Yolo Counties. The remaining five facilities with tracer detections in the initial testing were not retested because the owner/operators did not

[9] Federal Register, Vol. 53, No. 185, Friday September 23, 1988, p. 37086.

schedule retests. Retests are still ongoing in San Diego County and the city of Temecula. For 27 of the 34 systems, detectable quantities of tracer were found during the retest, confirming the conclusions of the original test. Retest results differed qualitatively (detect vs. non-detect) from the original test results in only 7 cases with 6 of the systems that previously had tracer releases yielding a non-detect result in the retest, typically following a system repair. In one case a system that had not had a tracer release in the original test had one in the subsequent test suggesting that a "repair" may have created rather than alleviated a problem. An example of such a repair might be over-tightening a fitting in a manner that damages an O-ring seal creating a pathway for a release.

Table 6 summarizes the results for the systems that were retested in Sacramento and Yolo Counties. Although the retest results show a slight improvement relative to the initial test results, more than 80% of the retested systems still release detectable quantities of a tracer. Failure to repair most of the vapor release sources may be attributed, in part, to the fact that contractors familiar with California Air Resources Board (CARB) testing standards and protocols were typically employed to institute corrective action. The CARB standard, test procedure (TP)-201.3 Static Pressure Performance (Leak Decay Test), is not as sensitive as the method used to evaluate UST systems in this project. In several cases, however, the source of the original tracer release appears to have been successfully identified and corrected. Tightening the seal at an automatic tank gauging cable penetration along the tank top changed one system from the "tracer detected" to the "no tracer detected" category. In another case, the original tracer detection may have resulted from activities related to a regularly scheduled CARB maintenance and testing event that occurred between inoculation and sample collection. This event did not recur during the retest and no detectable quantity of tracer was released.

Table 6. Comparison of change in maximum tracer concentrations observed for systems that were retested in Sacramento and Yolo Counties

Maximum tracer concentration T (µg/L)	Original test		Retest	
	Number [a]	Percent [b]	Number [a]	Percent [b]
T=ND	1	2.9	6	17.6
ND<T≤0.05	10	29.4	6	17.6
0.05<T≤0.5	13	38.2	12	35.3
0.5<T≤5.0	7	20.6	6	17.6
T>5.0	3	8.8	4	11.8

[a]Number of systems with the specified range of tracer concentrations during original test or retest

[b]Percent of systems with a specified result during original test or retest

Effects of Response Bias on the Results

The stratified random sampling design employed in this study was intended to provide a representative sample of UST systems so that accurate conclusions on release status could be drawn. The fact that 63% of the selected systems were not tested, largely because owner/operators refused access, raises questions about whether there might be systematic differences between systems that were tested compared with those that were not tested. Two testable distinctions between these groups relate to system design and ownership. No statistically significant difference ($p<0.05$) was observed in participation rates between double-walled, single-walled and hybrid UST systems. However, participation in the study was significantly higher among major oil companies than among independent distributors (54.4% vs. 23.6%; $p<0.01$). It is impossible to conclusively establish whether this response bias has affected the study results, but there was no statistically significant difference in tracer release detections between the major companies and independent distributors. The similarity between the results for the portion of each group that was tested suggests, but does not prove, that the untested portions of each population might have exhibited the same outcomes.

Conclusions

Liquid phase releases of petroleum products appear to be very rare (about 0.5% of tested cases) in all types of systems (single-walled, double-walled or hybrid) with the equipment required to meet current standards. Piping systems appear to be both liquid and vapor tight in the majority of cases, although the one liquid phase release was from a single-walled pressurized piping component. None of the test results was consistent with the suspicion of a liquid release from any tank, either double-walled or single-walled. However, vapor phase releases of tracers from tank components or connections occurred from more than 60% of the systems. The frequency of detectable tracer releases was statistically indistinguishable between double-walled, single-walled and hybrid systems. The similarity in the results for single and double-walled systems, combined with several other lines of evidence, suggests that common elements of system design, construction or installation along the tank top may be the source of these vapor phase releases.

The two largest tracer releases observed in this study (SY08 and TM16) were estimated to have been associated with product releases of about 0.02 gallons per hour (liquid equivalent) with virtually all of the remaining releases more than two orders of magnitude smaller. Thus, the largest observed vapor release is ten times smaller (as a liquid equivalent) than the regulatory standard for tank and line tightness test methods (0.2 gallons per hour). Current release detection monitoring approaches are not designed to detect vapor releases of any size. The upper limit of the estimate of the release rate associated with the only liquid product release indicated by the study was 50 times lower than the current standard suggesting that these systems could not detect the observed releases consistently even if operating precisely as designed. The only confirmed liquid release was smaller than the largest vapor releases, but similar in magnitude to the next largest group of vapor releases. Such small releases may be of environmental concern, especially with respect to MTBE that may selectively partition into pore water within the backfill and subsequently enter groundwater. The extent to which this is a problem obviously depends on the length of time the release has been occurring, the rate at which water infiltrates to the water table through the UST excavation zone, the efficiency of any

connection between shallow groundwater and groundwater used as a drinking water supply and the facility's proximity to drinking water wells. Comprehensive modeling studies should be undertaken to determine the impact of the frequent small releases observed in this study on groundwater quality.